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(54) **Rubber compositions**

Kautschukmischungen

Compositions de caoutchouc

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Description

[0001] This invention relates to rubber compositions and more particularly to a rubber composition suitable for use in pneumatic tires.

[0002] Carbon black is widely used as a reinforcing agent for rubber. In general, dibutyl terephthalate absorption (DBP) is within a range of 100-130 ml/100 g as an important colloidal property in the carbon black used. This is because, when the value of DBP is too small, the reinforcing effect is not obtained, while when it is too large, the resistance to fatigue failure may be lowered. In particular, when the carbon black is applied to a tread rubber, it frequently has a DBP of 100-120 ml/100 g.

[0003] Recently, silica has been used as a reinforcing agent for rubber from the viewpoints that the need for low fuel consumption is increased and the running performance on wet road surfaces is ensured.

[0004] However, when the case of compounding silica is compared with the case of compounding carbon black, it has the drawbacks that the shrinking quantity of unvulcanized rubber is increased to degrade the processability, and the dispersibility in the unvulcanized rubber becomes poor to degrade the wear resistance at a higher input after the vulcanization, and static electrification is likely to be caused.

[0005] Lately, it has been attempted to blend carbon black with silica in order to simultaneously establish low rolling resistance, good running performance on wet road surface and the like as advantages of silica and good wear resistance as an advantage of carbon black. In this case, DBP of the carbon black used is within the conventionally used range, so that the drawbacks of the silica can not sufficiently be overcome. Therefore, it is desired to further improve the above blending effect.

[0006] The present inventors have previously proposed rubber compositions simultaneously satisfying the requirements of rolling resistance and wear resistance with the use of carbon black having DBP exceeding the conventionally used range from the viewpoints of change of commercial needs and the advance of techniques of microscopically controlling carbon black. However, these rubber compositions do not necessarily satisfy all requirements of diversified tire performances.

[0007] On the other hand, the commercial needs of low fuel consumption are extended to all-season tires and high-performance tires in addition to general-purpose tires aiming at improved wear resistance. As a result, it is strongly demanded to develop a technique for improving various performances of the tires.

[0008] Attention is also drawn to the disclosures of:

i) Derwent Abstract AN 92-061826 and JP-A-4-008741;
ii) Derwent Abstract AN 92-056467 and KR-B-92-04783.

[0009] It is, therefore, an object of the invention to provide a rubber composition having improved properties required in tires or the like such as wear resistance, rolling resistance, running performance on wet road surface, processability, antistatic electrification and the like by compounding a particular carbon black and silica as a reinforcing agent for rubber to possess the advantages of both carbon black and silica while overcoming the disadvantages of both carbon black and silica in order to simultaneously realize the improvement of various tire performances and low fuel consumption.

[0010] According to the present invention, there is provided a rubber composition comprising 10-100 parts by weight of carbon black having a specific surface area of nitrogen adsorption (N_2SA) of 70-90 m^2/g, measured according to ASTM D3037-89, and a dibutyl terephthalate absorption (DBP) of 170-250 ml/100 g, measured according to ASTM D2414-90, and 10-100 parts by weight of silica, based on 100 parts by weight of diene rubber ingredient.

[0011] In a preferable embodiment of the invention, the carbon black has DBP of 170-200 ml/100 g.

[0012] In another preferable embodiment of the invention, a compounding ratio of carbon black to silica is 20/80 - 80/20, and particularly a total compounding amount of carbon black and silica is 40-160 parts by weight per 100 parts by weight of diene rubber ingredient.

[0013] In a further preferable embodiment of the invention, the silica has a surface area by cetyltrimethyl ammonium bromide process (CTAB) of 100-300 m^2/g, measured according to ASTM D3765-89, and DBP of 150-300 ml/100 g, measured according to ASTM D2414-90.

[0014] The rubber composition according to the invention is suitable for use in pneumatic tires, and is most preferably for use in a tread of the tire. However, it may be applied to other rubber portions of the tire such as one sidewall portion. When the tire tread is constructed of two different rubbers in the radial direction of the tire, the rubber composition according to the invention is usually used as a so-called outer cap rubber, but it may be used as a so-called inner base rubber.

[0015] As to the carbon black, when N_2SA is less than 70 m^2/g, the wear resistance is degraded, while when it exceeds 90 m^2/g, tan δ becomes large and hence the rolling resistance is undesirably degraded. Therefore, N_2SA of the carbon black is restricted to a range of 70-90 m^2/g.

[0016] On the other hand, when DBP is less than 170 ml/100 g, the dispersibility of silica is not improved, while when it exceeds 250 ml/100 g, it is technically difficult to produce and use such a carbon black. According to the invention, therefore, DBP of the carbon black is restricted to a range of 170-250 ml/100 g, more particularly 170-200 ml/100 g.

[0017] When the amount of carbon black compounded is less than 10 parts by weight based on 100 parts by weight of diene rubber ingredient, the effect of improving the dispersibility and wear resistance by the compounding of carbon black is less, while when it exceeds 100 parts by weight, the effect of simultaneously establishing the low rolling resistance and the improvement of the running performance on wet road surface with the addition of silica is less and also the wear resistance is undesirably lowered.

[0018] Similarly, when the amount of silica compounded is less than 10 parts by weight, the effect of improving the running performance on wet road surface by the compounding of silica is less, while when it exceeds 100 parts by weight, the rolling resistance and wear resistance are undesirably degraded.

[0019] In a preferred embodiment of the invention, when the compounding ratio of silica to carbon black is less than 20/80 (amount of silica is less), the effect of simultaneously establishing the low rolling resistance and the improvement of the running performance on wet road surface is less as mentioned above, while when it exceeds 80/20 (amount of carbon black is less), the dispersibility is undesirably lowered to degrade the wear resistance.

[0020] In this preferred case, when the total compounding amount of silica and carbon black is less than 40 parts by weight, sufficient reinforcing effect and running performance on wet road surface may not be obtained, while when it exceeds 160 parts by weight, the wear resistance and the rolling resistance begin to be degraded.

[0021] Moreover, when the silica to be compounded has a surface area by CTAB process of 100-300 m^2/g and DBP of 150-300 ml/100 g, a reinforcing property sufficient to improve the wear resistance is obtained and also it is effective to simultaneously establish good running performance on wet road surface and rolling resistance.

[0022] The interaction between silica and carbon black will be described below.

(1) The dispersibility of silica into polymer is poor as compared with the usually used carbon black owing to its particle size and property of surface functional group. Furthermore, the wear resistance at a large deformation region as in a tire mainly running on mountain and slope roads is poor, which results from the reinforcing mechanism in the polymer.

However, the dispersibility of silica is improved by combining with carbon black defined in the invention or high-structure carbon black. Furthermore, the high-structure carbon black is superior to the usually used carbon black in the followability at large deformation region and the reinforcing property. That is, the degradation of the wear resistance which is a drawback in the silica compounding is prevented by the addition of the high-structure carbon black.

(2) In the silica compounding, the hysteresis loss of the rubber composition becomes large in respect of large deformation as compared with the case of compounding the usually used carbon black, but is small in respect of slight deformation. This is advantageous to improve the running performance on wet road surface and reduce the rolling resistance.

(3) In general, the high-structure carbon black is known to have poor resistance to fatigue failure at repetitive input owing to its orientation. Since the silica compounding has excellent resistance to fatigue failure as compared with the carbon black, the drawback of the high-structure carbon black can be overcome by combining with the silica compounding.

(4) In the silica compounding, the electrical resistance properties of the rubber composition become large and cause static electrification through repetitive input (occurrence of static electricity). On the other hand, the high-structure carbon black according to the invention has high electrical conductivity as compared with the usually used carbon black and current easily flows (no storing of static electricity), so that the above drawback in the silica compounding can be eliminated by the compounding of the high-structure carbon black. Furthermore, the resistance to static electrification in the tire can be increased by increasing the compounding amount of the high-structure carbon black according to the invention.

(5) In the silica compounding, the shrinking quantity of unvulcanized rubber becomes large as compared with the compounding of usually used carbon black, so that the tackiness is poor and the processability is degraded. On the other hand, the high-structure carbon black according to the invention has small shrinking quantity as compared with the usually used carbon black and has a sufficient tackiness, so that the degradation of the processability in the silica compounding can be prevented by combining with the compounding of the high-structure carbon black.

(6) As mentioned above, the combination of the high-structure carbon black and silica according to the invention largely serves to improve the running performance on wet road surface and the reduction of the rolling resistance. Particularly, the dispersibility of silica is improved by such a combination to further reduce the rolling resistance.

[0023] The carbon black used in the invention can be produced by using a usual oil furnace as follows.

[0024] That is, a starting material of high aromatic ingredient having a uniform composition is sprayed into a narrow

region inside the furnace through a nozzle forming oil droplets at a smaller distribution. In this case, the reaction time can be equalized by making distributions of furnace temperature and combustion gas stream smaller, whereby the desired carbon black can be obtained (see sample 1 in Comparative Example 3 and Examples 1 and 2).

[0025] The following examples are given in illustration of the invention and are not intended as limitations thereof.

[0026] Various rubber compositions are prepared according to a compounding recipe shown in Table 1 and the dispersibility, volume resistivity, shrinking quantity, wear resistance, rolling resistance and running performance on wet road surface are evaluated with respect to each rubber composition as follows:

(1) Dispersibility

The evaluation of the dispersibility is conducted by measuring average particle size, total area and area ratio through SEM-IA (scanning electron microscope-image processing apparatus) process.

The smaller the value, the better the dispersibility.

Moreover, the measurement is carried out as follows:

A sample to be measured (tread rubber taken out from a tire) is cut in ethanol by means of a razor's edge cleaned with chloroform.

In order to ensure uniform cut sections, a new razor is used every sample.

Then, the cut sample is subjected to an electrically conducting treatment (carbon coater) to prepare a measuring specimen (size: 20 x 10 mm).

The specimen is photographed into two fields of reflected electron image (composition image) by SEM (magnification x 100, applied voltage: 25-30 kV).

In the photographing, a brightness of colour shading in background is set to 0 level (black), and a brightness of secondary electron (SEI) and reflected electron (BEI) detecting device is set so as to intensify a contrast.

The particle size, total area and area ratio are measured from the photograph by IA processing. Specifically, the particles included in a field of 900 x 1200 μm are counted, from which the particle size, total area and area ratio are evaluated. In this case, the measurement of each specimen are carried out at two fields, from which an average value is calculated for the evaluation. Moreover, the term "area ratio" means a ratio of the total area to a measuring field area.

As SEM and IA, commercially available general-purpose devices are used.

(2) Volume resistivity

It is measured by means of an ADVANTEST High Megohm Meter TR8601 (commercially available device).

(3) Shrinking quantity

A sample 30 cm in length is extruded through a MPT (Monsanto Processability Tester) at a shear rate of 153.63 l/sec and left to stand on talc for 24 hours, and thereafter the shrinking quantity with respect to the initial length of 30 cm is measured. The shrinking quantity of each sample is represented by an index value on the basis that Comparative Example 1 is 100.

The larger the index value, the smaller the shrinking quantity.

(4) Wear resistance

Each rubber composition is applied to a tread of a passenger car tire having a tire size of 195/65R15. Then, the tire is mounted onto a vehicle having an engine displacement of 2500 cc and actually run on a test course of general express road specification or mountain-slope road specification over a distance of 20000 km, and thereafter the depth of the remaining groove in the tread is measured. The measured value is represented by an index on the basis that Comparative Example 1 is 100. The larger the index value, the better the wear resistance.

(5) Rolling resistance (RR)

Each rubber composition is applied to a tread of a passenger car tire having a tire size of 195/65R15, which is mounted onto a rim of 6JJ under an internal pressure of 2.0 kgf/cm^2 and run on a drum at a speed of 80 km/h under a load of 440 kg and then the rotation of the drum is stopped, during which the rolling resistance is measured. The rolling resistance is represented by an index on the basis that Comparative Example 1 is 100. The larger the index value, the better the rolling resistance.

(6) Running performance on wet road surface (WET performance)

The test tire is mounted onto a trailer and run on a wet asphalt-paved road according to a method defined in UTQGS (tire quality grade standard) of USA, during which a friction resistance in the locking of tire rotation is measured. The measured value is represented by an index on the basis that Comparative Example 1 is 100. The larger the index value, the better the WET performance.

Table 1(a)

		Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4
Polymer		Tuf2530*1 96.25 BR01*2 30.0	Tuf2530 96.25 BR01 30.0	Tuf2530 96.25 BR01 30.0	Tuf2530 96.25 BR01 30.0
Carbon black N_2SA/DBP parts		N339 80/125 60.0	N110 140/115 60.0	sample 1 80/185 60.0	
Silica parts Coupling agent Si69*3					Nipsil AQ*8 60.0 6.0
Zinc white Stearic acid Antioxidant 6C*4 Wax Aromatic oil		3.0 2.0 1.5 1.0 5.0	3.0 2.0 1.5 1.0 5.0	3.0 2.0 1.5 1.0 5.0	3.0 2.0 1.5 1.0 5.0
Vulcanization accelerator	DM *5 DPG*6 NS *7	1.0 0.5 1.0	1.0 0.5 1.0	1.0 0.5 1.0	1.0 0.5 1.0
Sulfur		1.5	1.5	1.5	1.5
Dispersibility average particle size μm total area m^2 area ratio %					8.05 27300 1.41
Volume resistivity (Ωcm)		$\leq 10^8$	$\leq 10^8$	$\leq 10^8$	$\geq 10^{15}$
Index of shrinking quantity		100	120	120	30
Index of wear resistance general express road mountain-slope roads		100 100	110 112	119 116	148 75
RR index		100	81	110	132
Index of WET performance		100	108	102	120

Table 1(b)

		Comparative Example 5	Example 1	Example 2
Polymer		Tuf2530 96.25 BR01 30.0	Tuf2530 96.25 BR01 30.0	Tuf2530 96.25 BR01 30.0
Carbon black N_2SA/DBP parts		N339 80/125 30.0	sample 1 80/185 30.0	sample 1 80/185 40.0
Silica parts Coupling agent Si69*3		Nipsil AQ 30.0 3.0	Nipsil AQ 30.0 3.0	Nipsil AQ 40.0 4.0
Zinc white		3.0	3.0	3.0
Stearic acid		2.0	2.0	2.0
Antioxidant 6C*4		1.5	1.5	1.5
Wax		1.0	1.0	1.0
Aromatic oil		5.0	5.0	5.0
Vulcanization accelerator	DM *5	1.0	1.0	1.0
	DPG*6	0.5	0.5	0.5
	NS *7	1.0	1.0	1.0
Sulfur		1.5	1.5	1.5
Dispersibility average particle size μm total area m^2 area ratio %		6.25 23200 1.20	5.00 9800 0.51	5.48 19500 1.01
Volume resistivity (Ωcm)		≥ 1015	8.12×10^8	$\leq 10^8$
Index of shrinking quantity		50	98	110
Index of wear resistance general express road mountain-slope roads		138 92	145 128	142 131
RR index		127	130	128
Index of WET performance		112	115	118

*1: solution-polymerized SBR, Tuffden (trade name), made by Asahi Chemical Industry Co., Ltd.

*2: BR made by Japan Synthetic Ruber Co., Ltd.

*3: silane coupling agent, Si69 (trade name), made by DEGUSSA, bis-(3-triethoxysilylpropyl)-tetrasulfide

*4: N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylene diamine

*5: dibenzothiazyldisulfide

*6: diphenylguanidine

*7: N-tert-butyl-2-benzothiazyl sulfenamide

*8: CTAB: 184m^2/g, DBP: 200 ml/100 g

[0027] In the carbon black, N2SA is measured according to ASTM D3037-89, and DBP is measured according to ASTM D2414-90.

[0028] In the silica, CTAB is measured according to ASTM D3765-89 and DBP is measured according to ASTM D2414-90 after the removal of adsorbed water by heating at 200°C for 15 minutes.

[0029] As seen from the results of Table 1, the average particle size, total area and area ratio in each example becomes smaller than those of each comparative example, so that the dispersibility in the examples is improved. Moreover, the dispersibility is very poor in the case of compounding only silica (Comparative Example 4), while in Comparative Example 5 compounding silica and carbon black, the dispersibility is improved but is poorer than that of the examples because DBP of the carbon black is outside the range defined in the invention.

[0030] In the examples, the volume resistivity is equal or near to the values in the case of compounding no silica (Comparative Examples 1-3).

[0031] As to the shrinking quantity, the occurrence of the shrinking by the silica compounding (Comparative Examples 4, 5) are sufficiently prevented in the examples.

[0032] In the examples, the degradation of the wear resistance at the large deformation region by the silica compounding (course of mountain-slope road specification in Comparative Examples 4, 5) is sufficiently prevented, but also the wear resistance on the course of general express road specification is considerably improved.

[0033] In the examples, the rolling resistance is considerably improved as compared with the case of compounding no silica (Comparative Examples 1-3).

[0034] In the examples, the running performance on wet road surface is considerably improved as compared with the case of compounding no silica (Comparative Examples 1-3).

[0035] As mentioned above, according to the invention, rubber compositions possessing the merit of both carbon black and silica while compensating for the disadvantages of both carbon black and silica can be obtained by the combination of the high-structure carbon black and silica. That is, the dispersibility of the silica is improved to improve the wear resistance and decrease the shrinkage. Further, when such a rubber composition is applied to a tire tread, the processability is improved and tires having a low rolling resistance, excellent running performance on wet road surface and a long service life can be obtained.

Claims

1. A diene rubber composition comprising 10-100 parts by weight of carbon black having a specific surface area of nitrogen adsorption (N_2SA) of 70-90 m^2/g, measured according to ASTM D3037-89, and a dibutyl terephthalate absorption (DBP) of 170-250 ml/100 g, measured according to ASTM D2414-90, and 10-100 parts by weight of silica, based on 100 parts by weight of diene rubber ingredient.

2. A diene rubber composition as claimed in claim 1, characterized in that said carbon black has DBP of 170-200 ml/

100 g.

3. A diene rubber composition as claimed in claim 1 or 2, characterized in that a compounding ratio of carbon black to silica is 20/80 - 80/20, and a total compounding amount of carbon black and silica is 40-160 parts by weight.

4. A diene rubber composition as claimed in any of claims 1 to 3,
characterized in that said silica has a surface area by cetyltrimethyl ammonium bromide process (CTAB) of 100-300 m^2/g, measured according to ASTM D3765-89, and DBP of 150-300 ml/100g, measured according to ASTM D2414-90.

Patentansprüche

1. Dienkautschuk-Zusammensetzung, die aufweist: 10-100 Gewichtsteile Ruß mit einer spezifischen Oberfläche für Stickstoffadsorption (N_2SA) von 70-90 m^2/g, gemessen nach ASTM D3037-89, und einer Dibutylterephthalat-Absorption (DBP) von 170-250 ml/100 g, gemessen nach ASTM D2414-90, sowie 10-100 Gewichtsteile Siliciumdioxid, bezogen auf 100 Gewichtsteile Dienkautschuk-Bestandteil.

2. Dienkautschuk-Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß der Ruß einen DBP-Wert von 170-200 ml/100 g aufweist.

3. Dienkautschuk-Zusammensetzung nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß ein Mischungsverhältnis von Ruß zu Siliciumdioxid gleich 20/80-80/20 ist, und daß ein Gesamtmischungsanteil von Ruß und Siliciumdioxid 40-160 Gewichtsteile beträgt.

4. Dienkautschuk-Zusammensetzung nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß das Siliciumdioxid eine spezifische Oberfläche nach dem Cetyltrimethylammoniumbromid-Verfahren (CTAB) von 100-300 m^2/g, gemessen nach ASTM D3765-89, und einen DBP-Wert von 150-300 ml/100 g aufweist, gemessen nach ASTM D2414-90.

Revendications

1. Composition de caoutchouc diénique comprenant 10 à 100 parties en poids de noir de carbone ayant une surface spécifique d'adsorption d'azote (N_2SA) de 70-90 m^2/g, mesurée selon la méthode ASTM D3037-89, et une absorption de téréphtalate de dibutyle (DBP) de 170-250 ml/100 g, mesurée selon la méthode ASTM D2414-90, et 10 à 100 parties en poids de silice, sur la base de 100 parties en poids d'ingrédient de caoutchouc diénique.

2. Composition de caoutchouc diénique selon la revendication 1, caractérisée en ce que ledit noir de carbone a une DBP de 170-200 ml/100 g.

3. Composition de caoutchouc diénique selon la revendication 1 ou 2, caractérisée en ce que un rapport de mélange du noir de carbone à la silice est de 20/80 à 80/20, et une proportion totale de mélange du noir de carbone et de la silice est de 40 à 160 parties en poids.

4. Composition de caoutchouc diénique selon l'une quelconque des revendications 1 à 3, caractérisée en ce que ladite silice a une surface spécifique par le procédé au bromure de cétyltriméthyl ammonium (CTAB) de 100-300 m^2/g, mesurée selon la méthode ASTM D3765-89 et une DBP de 150-300 ml/100 g, mesurée selon la méthode ASTM D2414-90.